Reactions of Diterpenoids in Concentrated Sulphuric Acid. Part 1. Novel Rearrangements of Tetrahydroabietic Acids

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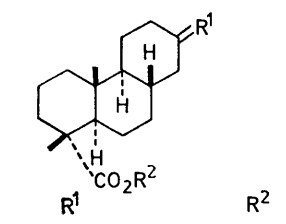
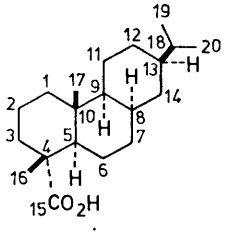
Dissolution of 8β,13βH-, 8β,13αH-, and 8α,13αH-tetrahydroabietic acids (1), (2), and (4), respectively, in cold concentrated sulphuric acid led to decarbonylation, followed by a novel skeletal rearrangement, and recarbonylation to give *inter alia* (±)-2βH,4aα,4bβ,8aα,10aβ-tetradecahydro-α,α,8,8-tetramethylphenanthren-2-ylacetic acid (5) and (±)-4aα,4bβ,8aα,10aβ-tetradecahydro-8,8-dimethyl-2ξ-(1-methylethyl)phenanthrene-2-carboxylic acid (12). The structures of these rearrangement products have been determined and preliminary experiments have indicated a possible mechanism for their formation.

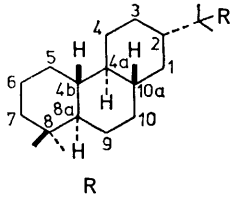
THE tetrahydroabietic acids (1), (2), and (4), which were required for this investigation, are well characterised [1,2] and the most readily available is the all-*trans*-isomer (1). The latter was prepared by the method of Burgstahler,[1] except that in our hands the lithium in liquid ammonia reduction of abietic acid only proceeded satisfactorily



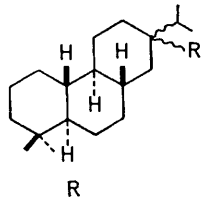
	R^1	R^2
(1)	α-$CHMe_2$, β-H	H
(2)	α-H, β-$CHMe_2$	H
(3)	α-$CHMe_2$, β-H	Me



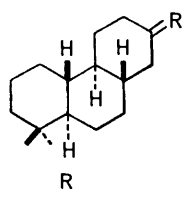
(4)



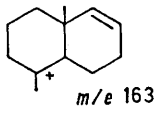
	R
(5)	CO_2H
(6)	CO_2Me
(7)	CH_2OH
(8)	COCl
(9)	NCO
(10)	NHMe
(11)	OEt



	R
(12)	CO_2H
(13)	CO_2Me
(14)	CH_2OH

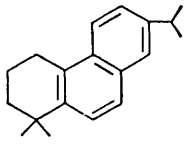


	R
(15)	CMe_2
(16)	H, 
(17)	O
(18)	α-COMe, β-H
(19)	α-$COCD_3$, β-D



m/e 163

(20)



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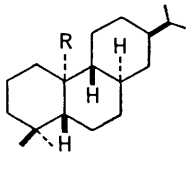
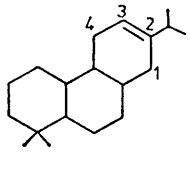
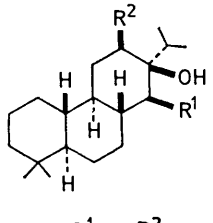


	R
(22)	CH_2OH
(23)	CO_2H

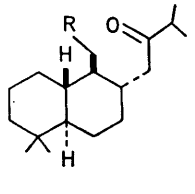


(24)

(25) Δ^1-isomer



	R^1	R^2
(26)	H	OH
(27)	OH	H



	R
(28)	CHO
(29)	CO_2H
(30)	CO_2Me

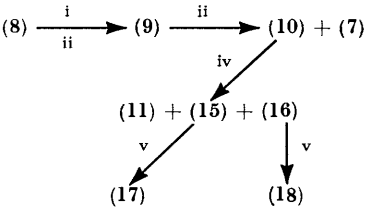
when the ether recommended as a co-solvent [1,3] was replaced by a mixture of tetrahydrofuran and t-butyl alcohol. The resultant mixture of dihydroabietic acids was converted [1] into the tetrahydro-acids (1) and (2). The isomeric acid (4) was prepared by hydrogenation [1,4] of abietic acid.

Dissolution of the all-*trans*-acid (1) [shown to contain 11% of its 13-epimer (2) by g.l.c. of its methyl ester] in concentrated sulphuric acid at 0 °C led to decarbonylation (*cf.* ref. 5). Nevertheless the yield of acidic products † was *ca.* 60% and increased to *ca.* 80% when the reaction was carried out in a solution saturated with carbon monoxide, indicating that recarbonylation was occurring. G.l.c. of the methyl esters of the crude acidic products revealed the presence of at least ten compounds. A crystalline acid (A), $C_{20}H_{34}O_2$, was isolated as the least polar band by chromatography of the mixture. A more polar band afforded an isomeric acid (B). The acid (A) was more readily isolated from the crude acidic mixture, in 15—20% yield, *via* its sparingly soluble sodium salt. The acids (A) and (B) which are shown in the sequel to have structures (5) ‡ and (12), respectively, were also separated by lithium aluminium hydride reduction of the methyl esters of the mixed acids in boiling ether for 1 h. Under these conditions the ester (6) gave the alcohol (7), but the more sterically hindered ester (13) was largely unchanged.

† For a preliminary account see ref. 6.

‡ Structures (5)—(19), (26)—(30), and (39) represent racemates.

The acid (5) was optically inactive (no o.r.d. or c.d.) and its n.m.r. spectrum revealed the presence of two tertiary methyl groups (τ 9.24 and 9.13) neither of which is deshielded by an adjacent carboxy-group, and a 6-H



SCHEME 1 Reagents: i, NaN_3; ii, 90 °C; iii, $LiAlH_4$; iv, EtOH–K_2CO_3–MeI, reflux; v, O_3

singlet at τ 8.89. The latter was consistent with the grouping $CMe_2{\cdot}CO_2H$. The ^{13}C n.m.r. spectrum of the ester (6), unlike that of the ester (3), contained no signals above δ 20.15, indicating that the steric compression of the methyl groups attached to ring A in the ester (3) had been relieved.[7]

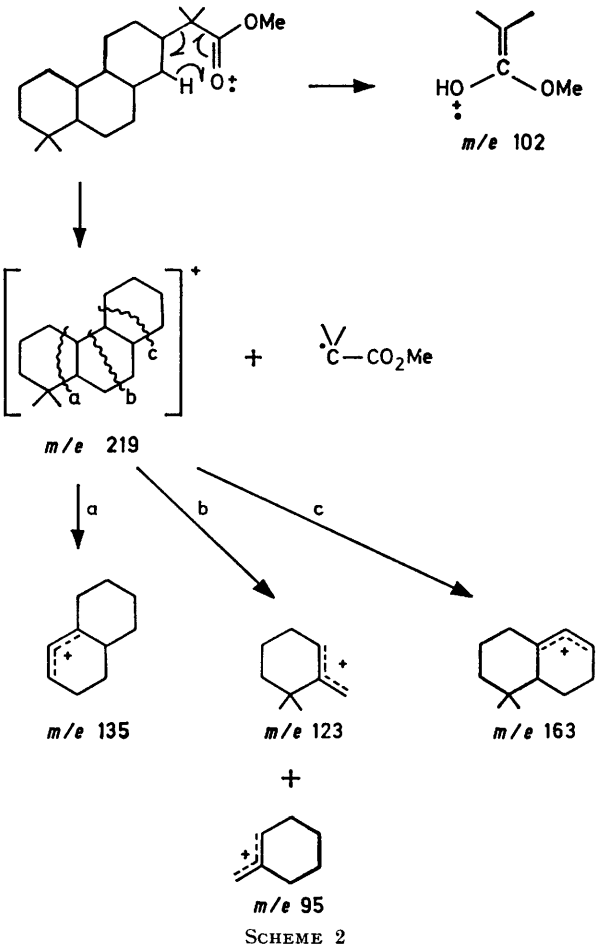
The structure of the side-chain in the acid (5) was established by degradation utilising the route in Scheme 1 (*cf.* ref. 8). Chromatography of the Hofmann elimination products on silver nitrate-impregnated alumina gave, in order of elution, the ether (11), the olefin (15), and the major olefin (16). The purity of the olefins was established by g.l.c. and their structures followed from their n.m.r. spectra (see Experimental section). Ozonolysis of the olefin (15) gave the six-ring ketone (17), $\nu_{max.}$ ($CHBr_3$) 1 709 cm^{-1}. Both the olefin (15) and the ketone (17) were optically inactive (no c.d. curves), thus confirming the lack of optical activity in the acid (5).

The mass spectra of the acid (5) * and its ester (6) supported the structures assigned to them. Thus the mass spectra of the methyl tetrahydroabietates show weak ions at $M - 43$, *i.e.* due to loss of the isopropyl group, but the direct loss of a methoxycarbonyl radical from the molecular ion appears to dominate the fragmentation process and leads to cleavage of ring C to give the ion (20) with *m/e* 163 as the base peak.[9] On the other hand the mass spectrum of the methyl ester (6) contained no peak corresponding to loss of an isopropyl group, but showed strong peaks at *m/e* 219 and 102 and the fragmentation pattern, which can be rationalised as shown in Scheme 2, is consistent with the skeleton of the acid (5).

Confirmation of the carbon skeleton of the acid (5) was provided by mild dehydrogenation with palladised charcoal which afforded retene and simonellite (21). The latter was identified by comparison with an authentic specimen.[10]

The above degradations complete the elucidation of the structure of the acid (5) without regard to stereochemistry. The configuration of the side-chain was determined by examination of the methyl ketone (18). The ketone was unchanged (g.l.c.) after treatment with methanolic potassium hydroxide, although enolisation was shown to occur on reaction of the ketone with potassium hydroxide in tetrahydrofuran–deuterium oxide. In this case the product also gave only one peak of unchanged retention time on g.l.c., but its mass spectrum showed a molecular ion at *m/e* 266, corresponding to the introduction of four deuterium atoms; in support the n.m.r. spectrum of the deuterio-ketone (19), unlike that of the ketone (18), did not exhibit a signal at τ 7.88. Hence the methyl ketone grouping was assigned the equatorial orientation. The stereochemistry of the nucleus has not been directly determined, but was provisionally assigned the all-*trans*-skeleton on mechanistic considerations (see below).

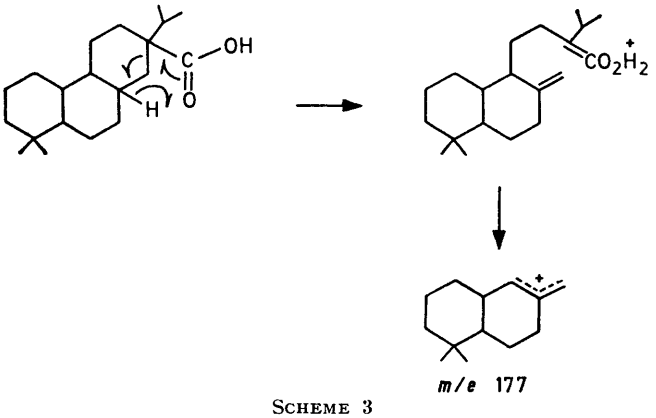
The rearrangement acid (12) was a much weaker acid than its isomer (5), and partial separation from the latter could be achieved by extraction with 0.25N-sodium hydroxide solution, when the acid (12) tended to remain in the organic layer. A more convenient and complete separation was accomplished by hydride reduction of the mixed methyl esters (see above). The resultant ester (13) was resistant to hydrolysis, but was reduced by refluxing with lithium aluminium hydride in ether for 24 h to give the alcohol (14). Oxidation of the latter with Jones reagent gave the optically inactive acid (no c.d. or



SCHEME 2

* The mass spectrum fragmentation patterns of the tetrahydroabietic and related acids have been found to be almost identical with those of their corresponding methyl esters.

o.r.d. curve) (12) whose n.m.r. spectrum showed an isopropyl doublet at τ 9.08 and two tertiary methyl groups (τ 9.23 and 9.13). The latter were assigned to a *gem*-dimethyl grouping at C-8, by analogy with the structure and n.m.r. data of the acid (5). The mass spectrum of the acid (12) differed considerably from that of its isomer (5). It showed a peak at *m/e* 263 corresponding to loss of an isopropyl group, but the dominant ion occurred at *m/e* 177 and could arise by fragmentation of ring C (see Scheme 3).



SCHEME 3

The steric hindrance of the carboxy-group in the acid (12) suggested that it was tertiary, but failed to establish its location. On the assumption that this acid has the same carbon skeleton as the acid (5), the carboxy-group could be located at one of five positions, *viz.* 2, 4a, 4b, 8a, or 10a. The alcohol (22) is known,[11] but differs (n.m.r. spectrum) from the alcohol (14), hence excluding structure (23) for the acid. Three of the four remaining possible structures were eliminated by degradation. Decarboxylation of the acid (12) with lead tetra-acetate–copper(II) acetate in refluxing benzene and pyridine (*cf.* ref. 12) gave the three olefins (24), (25), and (15) in the ratio *ca.* 8 : 3 : 1 as determined by g.l.c. and n.m.r. data (see Experimental section). The yield of exocyclic olefin (15) was unusually low,[13] and this may be, in part, due to its undergoing cleavage to give the ketone (17) (*ca.* 10% yield), identical in all respects with the specimen prepared from the acid (5). Hence the structure of the acid, without regard to stereochemistry, must be (12).

Osmylation of the mixture of olefins gave two major diols. The n.m.r. spectrum of the more polar diol showed the 3-H as a double doublet at τ 6.37 in which the larger coupling of 11 Hz indicates a 1,2-diaxial relationship with 4-H. Hence the hydroxy at C-3, and also that at C-2, must have the β-configuration as in structure (26). The structure of the other diol also followed from its n.m.r. spectrum, in which the isopropyl methyls appeared as doublets at τ 9.12 and 9.07, and 1-H as a doublet at τ 6.81 with a coupling (J 9.5 Hz) characteristic of diaxial splitting. The diol must therefore have structure (27). Cleavage of the diol (26) with lead tetra-acetate gave the keto-aldehyde (28) which autoxidised during purification to give the acid (29). In the n.m.r. spectrum of the latter, the isopropyl methyl doublet had shifted downfield to τ 8.92 indicating that the compound contained an isopropyl ketone group. The presence of the latter was rigorously established by the n.m.r. spectrum of the methyl ester (30), which showed the isopropyl group at τ 8.93, and a five-proton complex multiplet at τ 7.25—7.65, assigned to the protons α to the carbonyl groups; irradiation at the frequency of the signal at τ 7.5 caused the isopropyl methyl doublet to collapse to a singlet. These results are only consistent with a diol of structure (26) and confirm the structure of the acid (12).

During the crystallisation of large quantities of the acid (5), a third isomeric acid, $C_{20}H_{34}O_2$, was isolated in small yield. Its mass spectrum did not contain a peak corresponding to the loss of an isopropyl group, but like that of the acid (5), contained strong peaks at *m/e* 219 and 88, thus suggesting the loss of the side-chain $CMe_2 \cdot CO_2H$ (see Scheme 2). Further evidence for this side-chain was provided by the n.m.r. spectrum of the acid which showed a 6 H singlet at τ 8.88. However only one other methyl group signal could be detected (as a sharp singlet at τ 9.28) which suggested that the third acid differed from the other two in ring A. The use of the shift reagent, $Eu(fod)_3$, on the alcohol derived by reducing the third acid with lithium aluminium hydride showed a large downfield shift of the side-chain methyl groups, but failed to clarify the position of the other methyl group. The c.d. of the third acid, and of its derived alcohol, showed very small positive dichromisms which probably indicates that the compounds are optically inactive, but cannot be regarded as conclusive. A possible structure for the acid is discussed below.

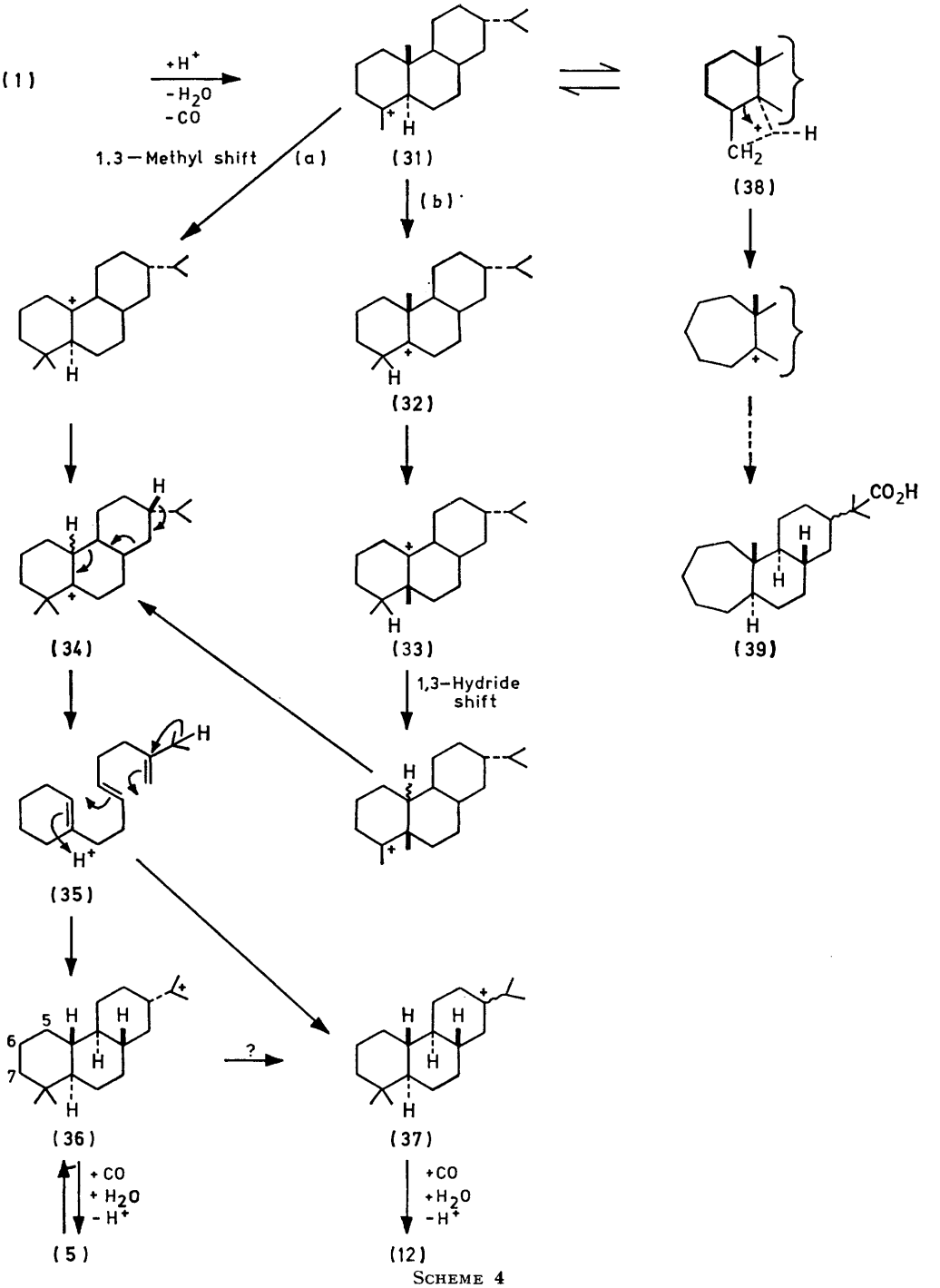
Examination by g.l.c. of the purified neutral products from the rearrangements revealed the presence of at least five components and the n.m.r. spectrum of the mixture showed no vinylic proton signals. Since the mass spectrum showed a molecular ion at *m/e* 262 (*i.e.* $C_{19}H_{34}$), and no peak at *m/e* 260, it was concluded that the mixture consisted of saturated hydrocarbons. The latter presumably arise by hydride ion abstraction by the intermediate carbonium ion(s) (see Scheme 4) from other diterpenoid derivatives present in the mixture.

To investigate the effect of stereochemistry on the rearrangement of the tetrahydroabietic acids, the isomers (2) and (4) were treated with sulphuric acid in the normal way. In each case analysis of the methyl esters of the crude acidic products by g.l.c. gave similar patterns of peaks to those obtained from the acid (1). Furthermore the rearranged acid (5) was isolated from both reactions. Hence it would appear that the stereochemistry of the tetrahydroabietic acid has little effect on the course of the rearrangement.

Examination of the products from a number of rearrangements of the acid (1) in cold concentrated sulphuric acid (by g.l.c. analysis of the methyl esters), showed that a similar mixture of acids was always produced in about the same proportions. It was concluded that a state of equilibrium was reached in the reaction medium, and that the numerous carbonium

ions involved in the rearrangements (see Scheme 4) only reacted with carbon monoxide to give the thermodynamically more stable acids.

In an attempt to change the relative stability of the carbonium ions, the rearrangement of the acid (1) was carried out in fluorosulphonic acid–antimony pentafluoride at 0 °C.[14] A vigorous reaction occurred and the resultant acidic product was isomeric with the starting acid (*m/e* 306), but analysis of the methylated products by g.l.c. showed that it contained at least thirteen esters of short retention times, none of which corresponded to the rearrangement products obtained using sulphuric acid at 0 °C. Furthermore, the n.m.r. spectrum of the mixture did not show an isopropyl doublet, indicating that a complex rearrangement involving the isopropyl group had occurred. The neutral fraction, unlike that obtained with sulphuric acid at 0 °C, was shown by mass spectrometry to contain a mixture of saturated and un-



SCHEME 4

saturated hydrocarbons. When the temperature of the mixture was reduced to −70 °C, and liquid sulphur dioxide was added to reduce the viscosity of the solution, very little reaction occurred, whilst at −30 °C the methylated acidic product was shown by g.l.c. to contain both starting material and compounds of short retention times.

The reaction of the tetrahydro-acid (1) in concentrated sulphuric acid at room temperature was also examined. In this case the acidic products were intractable and were shown by g.l.c. to be completely different from those obtained at 0 °C. The n.m.r. spectrum of the former did not show an isopropyl group doublet, indicating that a complex skeletal rearrangement had occurred.

The decarbonylation of several diterpene derivatives under acid conditions has been examined,[5] but little attention has been paid to the acidic products. The reaction of the tetrahydroabietic acids (1), (2), and (4) with cold concentrated sulphuric acid to give the isomeric acids (5) and (12) must take place *via* a decarbonylation–recarbonylation mechanism.[15,16] A novel skeletal rearrangement also appears to be involved since the products are racemic despite the presence of six asymmetric centres in the tetrahydro-acids. A possible mechanism was proposed [6] which satisfactorily accounted for these observations. This mechanism is shown in more detail in Scheme 4. Decarbonylation of the acid (1) affords the carbonium ion (31) which by either route (a) involving a 1,3-methyl shift [17] and a 1,2-hydride shift, or route (b) *via* a series of unexceptional shifts, affords the carbonium ion (34). Ring-opening of the latter would give the triene (35), which lacks asymmetry, and on protonation could cyclise to the carbonium ions (36) and (37). Carbonylation of the former would afford the acid (5), whilst carbonylation of the latter would yield the acid (12). By analogy with the acid-catalysed cyclisation of monocyclic polyolefins,[18] the cyclisation of the triene (35) would be expected to be stereospecific and lead to the all-*trans* products (5) and (12).

Rigorous proof of the decarbonylation–recarbonylation process (*cf.* ref. 16) was obtained by carrying out the rearrangement of the acid (1) in the presence of ^{14}C-labelled carbon monoxide; the product (5) was found to be highly radioactive. Evidence that the rearrangement takes place by a non-concerted mechanism, probably involving a series of equilibrating intermediate carbonium ions,[19,20] was obtained when the rearrangement of the acid (1) was carried out in cold deuteriosulphuric acid. The mass spectrum of the acid (5), isolated from this reaction, showed a peak of highest mass at *m/e* 335 corresponding to the incorporation of 29 deuterium atoms. Similarly the mass spectrum of its methyl ester showed the heaviest molecular ion at *m/e* 349. The pattern of the 30 molecular ions in these mass spectra was unusual; the intensities of the ions showed two maxima, one corresponding to the incorporation of 5—6 deuterium atoms and the other due to ions containing 22—23 deuterium atoms. The minimum in the intensity distribution occurred at *ca.* $M + 13$. In other examples of polydeuteriation, resulting from skeletal rearrangements *via* carbonium ions, a series of molecular ions with only one point of maximum intensity at about the centre of the group of ions has been reported.[19,20] The presence of two maxima presumably indicates greater complexity in the mechanistic pathways. The n.m.r. spectrum of the methyl ester (6) of the polydeuteriated acid, in which the methoxy group served as an internal standard showed that the isopropyl and *gem*-dimethyl groups were extensively deuteriated and that the deuterium content of the 8α- and 8β-methyl groups was almost identical. The mass spectrum of the deuteriated ester (6) showed a comparatively weak peak at *m/e* 102 but intense peaks at *m/e* 103—109, thus establishing the presence of up to seven deuterium atoms in the McLafferty rearrangement fragment (see Scheme 2).

The mechanism shown in Scheme 4 is consistent with the incorporation of a large number of deuterium atoms by deprotonation and reprotonation of the intermediate carbonium ions, but would not readily explain proton exchange in the methyl group which originated at C-10. However, deuteriation of this group could occur if the rearrangement of the ion (32) to (33), takes place *via* edge-protonated cyclopropanes (*cf.* ref. 19). The four protons which do not undergo exchange are presumably those attached to C-6 and -7 and they appear in the n.m.r. spectrum of the acid as a poorly resolved triplet at τ 8.58.

A small amount of the third acid was also isolated from the reaction in deuteriosulphuric acid. The mass spectrum of its methyl ester gave weak molecular ions at high mass numbers; nevertheless ions at all whole-number masses from *m/e* 320 to 346 were discernible, *i.e.* corresponding to the presence of up to 26 deuterium atoms. A possible structure for the ' third ' acid arises from consideration of the mechanism in Scheme 4. The ion (31) might be in equilibrium with the edge-protonated cyclopropane (38), which could rearrange to give a carbonium ion with a seven-membered ring A. If rings B and C in the latter opened, in a manner analogous to that shown in Scheme 4 for the ion (34), it would give a triene which on reprotonation could cyclise and then carbonylate to give the acid (39). Such a structure is compatible with the n.m.r. spectrum of this acid (see above).

Not unexpectedly the acid (5) was stable in concentrated sulphuric acid at 0—5 °C for 1 h. However when the solution was kept for 26 h, although most of the acid was recovered, g.l.c. analysis revealed that about eight acids had been formed and that the major product was the isomer (12). Repetition of this reaction in deuteriosulphuric acid led to the recovery of most of the acid (5), in which no deuterium could be detected by mass spectroscopy. The isomeric acid (12) was isolated and the mass spectra of the acid and its methyl ester revealed that they contained 29 deuterium atoms. The n.m.r. spectra of the acid and of its methyl ester showed that the isopropyl methyl groups had been completely deuteriated

and that the *gem*-dimethyl groups were heavily deuteriated. The extensive deuteriation of the acid (12) suggests that it arises *via* a series of carbonium ions similar to those involved in the formation of the acid (5). For example, decarbonylation of the latter followed by a 1,2-hydride shift would afford the ion (37) which by reversal of the ring-closure process shown in Scheme 4 could give the triene (35). Recyclisation of the latter followed by recarbonylation could then afford the acid (12). However the rearrangement must involve a more complex mechanism because such a pathway (a) fails to account for the deuteriation of the *gem*-dimethyl groups, and (b) would be expected to give rise to deuteriated acid (5). It is obvious that much further work is required to clarify the details of the mechanistic pathways from the tetrahydroabietic acids to the acids (5) and (12).

EXPERIMENTAL

Column chromatography was carried out on silica gel (Sorbsil M60; Crossfield), alumina (B.D.H.; neutral; grade 1), and Kieselgel G (Merck). T.l.c. was performed on layers of Kieselgel G or Kieselgel GF_{254} and the latter absorbent was used for p.l.c.

M.p.s were determined with a Kofler hot-stage apparatus and were corrected. U.v. spectra were measured for ethanol solutions with a Unicam SP 800 spectrometer. Unless otherwise stated, i.r. spectra were recorded as Nujol mulls with Unicam SP 1000 and Perkin-Elmer 125 and 157-G spectrometers.

N.m.r. spectra were determined for solutions in deuteriochloroform (internal tetramethylsilane) with Varian A 60A, Perkin-Elmer R 32, and Bruker HF3 instruments. Fourier-transform ^{13}C n.m.r. spectra were measured in deuteriochloroform at 22.62 MHz on a Bruker HF3 instrument with tetramethylsilane as internal standard.

Mass spectra were recorded with an A.E.I. MS902 instrument and optical rotations were measured for solutions in chloroform with a Thorn Bendix automated polarimeter type 243. A Varian 1527B instrument with a stainless steel column (150 × 0.3 cm o.d.) packed with 5% Carbowax on 80—100 Anakrom at a column temperature of 175—190 °C and a nitrogen flow of 30 ml min^{-1}, was employed for g.l.c. and all the analyses on acidic components were conducted on the derived methyl esters.

Light petroleum had b.p. 60—80 °C.

8β,13βH-*Tetrahydroabietic Acid* (1) (cf. *ref.* 1).—Abietic acid di-n-amylamine salt (50 g), suspended in dry tetrahydrofuran (250 ml) and t-butyl alcohol (250 ml), was added in portions over 15 min to a vigorously stirred solution of lithium (6 g) in distilled liquid ammonia (500 ml). Isolation of the products in the usual way [1] gave a mixture of 13βH-$\Delta^{8(14)}$-dihydroabietic acid (85%) and Δ^{13}-dihydroabietic acid (15%) (14.5 g), m.p. 182—183°.

Hydrogenation [1] of the mixed dihydro-acids followed by crystallisation from acetone gave the tetrahydroabietic acid (1), containing 11% of its 13-epimer (2), m.p. 177—181° (lit.[1] 180—181.5°), which was used in subsequent experiments. Its methyl ester (3) showed δ_C 14.6 (C-20), 16.6 (C-19), 18.2 (C-2), and 24.5 (C-16 and -17).

Reaction of 8β,13βH-*Tetrahydroabietic Acid* (1) *with Concentrated Sulphuric Acid.*—(a) *At* 0—5 °C. Tetrahydroabietic acid (2 g), shown to contain 11% of its 13-epimer by g.l.c., was finely powdered and added to a stirred solution of concentrated sulphuric acid (16 ml) at 0—5 °C. The latter had been previously saturated with carbon monoxide, generated *in situ* by the addition of sodium formate (250 mg). The solution was stirred at 0—5 °C for 45 min and then poured onto ice (50 g). The products were recovered in ether and separated into acidic (1.67 g) and neutral fractions (0.31 g) with 0.25N-sodium hydroxide solution. The crude acid crystallised from acetone as amorphous lumps which were used in the subsequent operations.

(i) *Chromatographic separation of the acids* (5) *and* (12). The acidic mixture (64 mg) was separated by p.l.c. with five developments in benzene–formic acid (99 : 1). Material from the less polar band (22 mg) was recovered in acetone and was recrystallised from acetone to give (±)-2βH,4aα,4bβ,8aα,10aβ-*tetradecahydro*-α,α,8,8-*tetramethylphenanthren*-2-*ylacetic acid* (5) as rectangular prisms, m.p. 212—214°, $[\alpha]_D^{25}$ 0° (*c* 0.3), no c.d. or o.r.d. curve (Found: C, 78.5; H, 11.1%; *m/e*, 306. $C_{20}H_{34}O_2$ requires C, 78.4; H, 11.2%; *M*, 306), $\nu_{max.}$ 2 640 and 1 690 cm^{-1}; τ (90 MHz) 9.24 (3 H, s, 8-Me), 9.13 (3 H, s, 8-Me), and 8.89 (6 H, s, C*Me*$_2$·CO_2H); τ ([$^2H_5$]pyridine; 90 MHz), 9.23 (3 H, s, 8-Me), 9.14 (3 H, s, 8-Me), and 8.66 (6 H, s, C*Me*$_2$·CO_2H).

Its *methyl ester* (6), prepared with diazomethane, crystallised from methanol as prisms, m.p. 78—80° (Found: C, 78.4; H, 11.25%; *m/e*, 320. $C_{21}H_{36}O_2$ requires C, 78.7; H, 11.3%; *M*, 320), $\nu_{max.}$ ($CHBr_3$) 1 720 cm^{-1}; τ 9.24 (3 H, s, 8-Me), 9.14 (3 H, s, 8-Me), 8.90 (6 H, s, C*Me*$_2$·CO_2Me), and 6.36 (3 H, s, OMe); δ_C 20.15 (8β-Me), 22.0 (C*Me*$_2$·CO_2Me), and 178.8 (C=O).

Material from the band of lower R_F (30 mg) was crystallised from acetone to afford (±)-4aα,4bβ,8aα,10aβ-*tetradecahydro*-8,8-*dimethy*-2ξ-(1-*methylethyl*)-2-*phenanthrene*-2-*carboxylic acid* (12) as prisms, m.p. 178—179°, $[\alpha]_D^{25}$ 0° (*c* 0.3), no c.d. or o.r.d. curve (Found: C, 78.65; H, 10.9%; *m/e*, 306. $C_{20}H_{34}O_2$ requires C, 78.4; H, 11.2%; *M*, 306), $\nu_{max.}$ 2,650 and 1 695 cm^{-1}; τ 9.23 (3 H, s, 8-Me), 9.13 (3 H, s, 8-Me), and 9.08 (6 H, d, *J* 6 Hz, CH*Me*$_2$).

The neutral fraction (0.68 g) from a similar rearrangement was chromatographed on silica gel (35 g). Elution with light petroleum afforded an oil (282 mg) which distilled at 80 °C (bath) and 0.5 mmHg (Found: C, 86.75; H, 13.5%; *m/e* 262. $C_{19}H_{34}$ requires C, 86.9; H, 13.1%; *M*, 262).

G.l.c. of the distillate revealed the presence of at least five hydrocarbons; its n.m.r. spectrum showed no olefinic proton signals.

(ii) *Chemical separation of the acids* (5) *and* (12). The mixed methyl esters (144 mg) (prepared with diazomethane) in ether (10 ml) were added to a refluxing stirred suspension of lithium aluminium hydride (20 mg) in ether (15 ml) and the reaction was continued for 1 h. Recovery of the products in the usual way gave a gum shown by t.l.c. to contain some starting ester and two reduction products. The mixture was purified by p.l.c. in ethanol–benzene (1 : 99) and two developments separated the ester from the unresolved reduction products.

The band of higher R_F was recovered as an oil (73 mg) which afforded the *methyl ester* (13) as prisms on crystallisation from methanol, m.p. 76—77° (Found: C, 78.45; H, 11.55%; *m/e*, 320. $C_{21}H_{36}O_2$ requires C, 78.7; H, 11.3%; *M*, 320), $\nu_{max.}$ ($CHBr_3$) 1 710 cm^{-1}; τ 9.25 (3 H, s, 8-Me), 9.16 (6 H, d, *J* 6 Hz, CH*Me*$_2$), 9.15 (3 H, s, 8-Me), and 6.32 (3 H, s, OMe); δ_C 17.8 (CH*Me*$_2$), 20.15 (8β-Me), and 176.8 (C=O).

The more polar band was recovered and further purified

by p.l.c. Seven developments with ethanol–benzene (1 : 99) resolved the two components. Material from the band of higher polarity was crystallised from light petroleum to yield (±)-2βH,4aα,4bβ,8aα,10aβ-*tetradecahydro*-α,α,8,8-*tetramethylphenanthren*-2-*ylethanol* (7) as prisms, m.p. 126—127° (Found: C, 82.0; H, 12.2%; *m/e*, 292. $C_{20}H_{36}O$ requires C, 82.1; H, 12.4%; *M*, 292), $\nu_{max.}$ 3 350 cm^{-1}; τ 9.22 (3 H, s, 8-Me), 9.18 (6 H, s, CMe_2·CH_2OH), 9.13 (3 H, s, 8-Me), and 6.64 (2 H, s, CH_2OH).

Material from the band of higher R_F was crystallised from light petroleum, to give (±)-4aα,4bβ,8aα,10aβ-*tetradecahydro*-8,8-*dimethyl*-2ξ-(1-*methylethyl*)*phenanthren*-2-*ylmethanol* (14) as cubes, m.p. 107—109° (Found: C, 82.3; H, 12.6%; *m/e*, 292. $C_{20}H_{36}O$ requires C, 82.1; H, 12.4%; *M*, 292), $\nu_{max.}$ 3 360 and 1 050 cm^{-1}; τ 9.23 (3 H, s, 8-Me), 9.14 (3 H, s, 8-Me), 9.14 (6 H, d, *J* 6 Hz, $CHMe_2$), and 6.39 (2 H, s, CH_2OH).

(iii) *Isolation of the acid* (5) *as its sparingly soluble sodium salt.* Tetrahydroabietic acid (8 g), shown to contain 8% of its 13-epimer by g.l.c. and *ca.* 25% of 13αH-$\Delta^{8(9)}$-dihydroabietic acid by mass spectrometry, was treated with sulphuric acid (65 ml) at 0 °C in the presence of sodium formate (500 mg) as in (i). The products were recovered in ether and the ethereal extracts were washed with an excess of 0.25N-sodium hydroxide to give a precipitate which was collected by filtration and suspended in water. The suspension was acidified with dilute hydrochloric acid and extracted with ether. Recovery afforded a solid (780 mg) which was crystallised from acetone to give the acid (5) as prisms, m.p. 211—213°, identical (i.r. spectrum and g.l.c.) with the specimen prepared in (i).

(iv) *Isolation of the third isomeric acid.* The crude acidic fraction (4.45 g) from (iii) was methylated with diazomethane and the mixture of esters in ether (35 ml) was reduced with lithium aluminium hydride and worked up as in (ii).

The crude product (3.79 g) was chromatographed on silica gel (150 g). Elution with ethyl acetate–light petroleum (1 : 49) afforded a mixture of methyl esters (1.14 g). Elution with ethyl acetate–light petroleum (1 : 24 and 3 : 47) yielded a mixture of alcohols (1.7 g) which was dissolved in acetone (70 ml) and treated with an excess of Jones reagent for 2.5 h at room temperature. The product, isolated in the usual manner, crystallised from acetone as microcrystals (157 mg) shown by g.l.c. analysis to be a mixture of 36% acid (5) and 60% of a third acid.

The mixed acids were separated by fractional crystallisation from acetone and the first crop was the acid (5), m.p. 212—214°, identical (i.r. spectrum and g.l.c.) with the specimen prepared in (i). Later crops were rich in the third acid and were recrystallised from acetone to give prisms (47 mg) of the third isomeric *acid* (homogeneous by g.l.c.), m.p. 189—191°, c.d. (*c* 0.001 7 in MeOH), $[\theta]_{250}$ 0°, $[\theta]_{216}$ + 22°, $[\theta]_{200}$ 0° (Found: C, 78.7; H, 11.25%; *m/e*, 306. $C_{20}H_{34}O_2$ requires C, 78.4; H, 11.2%; *M*, 306), $\nu_{max.}$ 2 670 and 1 702 cm^{-1}; τ (90 MHz) 9.30 (3 H, s, Me) and 8.88 (6 H, s, CMe_2·CO_2H).

The g.l.c. retention times of the esters (13) and (6) and of the methyl ester of the ' third acid ', at a column temperature of 175°, were 9.6, 12.8, and 16.0 min respectively.

(b) *At* 30 °C. The acid (235 mg), (containing 11% of its 13-epimer) was added to concentrated sulphuric acid (4 ml) and sodium formate (25 mg) at 30 °C and the solution was stirred for 1 h. Work-up in the normal fashion afforded an acidic fraction (76 mg) and a neutral fraction (151 mg) (Found: *m/e*, 262. $C_{19}H_{34}$ requires *M*, 262).

G.l.c. analysis of the acidic fraction showed that a complex mixture of acids had been produced which was totally dissimilar to that obtained from reactions carried out at 0—5 °C. There was no $CHMe_2$ doublet in the n.m.r. spectrum.

Reaction of the Tetrahydroabietic Acid (1) *with Concentrated Sulphuric Acid in the Absence of Sodium Formate.*—The acid (2 g), containing 10% of its 13-epimer, was treated with concentrated sulphuric acid (16 ml) at 0—5 °C, as in (a) above, except that the sodium formate was omitted. The products were separated into acidic (1.26 g) and neutral fractions (0.68 g) and each fraction gave the same results on purification as were obtained in (a) (iii).

Attempted Hydrolysis of the Methyl Ester (13).—The ester (41 mg) and potassium hydroxide (250 mg) in ethanol (15 ml) were stirred under reflux in an atmosphere of nitrogen for 23 h. The recovered material was shown by t.l.c. to be starting material.

Lithium Aluminium Hydride Reduction of the Methyl Ester of the ' Third ' Isomeric Acid.—The acid (39 mg) was methylated with diazomethane and the ester in ether (10 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (30 mg) in ether (15 ml). Stirring was continued at room temperature for 1 h, and the product was isolated in the usual way. Crystallisation from light petroleum yielded the *alcohol* as prisms, m.p. 121—122° (Found: C, 81.65; H, 12.25%; *m/e*, 292. $C_{20}H_{36}O$ requires C, 82.1; H, 12.4%; *M*, 292), $\nu_{max.}$ 3 310 and 1 040 cm^{-1}; τ 9.31 (3 H, s, Me), 9.20 (6 H, s, CMe_2·CH_2OH), and 6.62 (2 H, s, CH_2OH).

Lithium Aluminium Hydride Reduction of the Methyl Ester (13).—The ester (41 mg) in ether (10 ml) was added to a stirred suspension of an excess of lithium aluminium hydride (75 mg) in ether (10 ml) and refluxed for 24 h. Recovery in ether in the usual manner gave a solid (40 mg) which crystallised from light petroleum to yield the alcohol (14) as cubes, m.p. 106—108°, identical (i.r. and mass spectra) with the specimen prepared above.

Oxidation of the Alcohol (7).—The alcohol (45 mg) in acetone (15 ml) was treated with an excess of Jones reagent at room temperature for 2.5 h. The solution was diluted with water, the acetone was removed *in vacuo*, and the residue was extracted with ether. Recovery gave the acid (5) which crystallised from acetone as prisms, m.p. 212—214°, identical (i.r. spectrum) with the sample prepared above.

Oxidation of the Alcohol (14).—Excess of Jones reagent was added to a stirred solution of the alcohol (363 mg) in acetone (30 ml) at room temperature over 1 h and stirring was continued for a further 1.5 h. Recovery in ether afforded the acid (12) which crystallised from acetone as prisms, m.p. 177—178°, identical (i.r. spectrum) with the specimen prepared above.

Preparation of the Isocyanate (9).—The acid (5) (2.0 g) was treated with thionyl chloride (5 ml) in benzene (20 ml) under reflux for 5 h. Evaporation *in vacuo* gave the acid chloride (8) as a gum, $\nu_{max.}$ 1 790 cm^{-1}.

The latter in acetone (17 ml) at 0 °C was added to a solution of sodium azide (1.5 g) in water (1.5 ml) and shaken vigorously for 20 min. The mixture was poured into water and the product was recovered in xylene. The extract was dried and was heated at 90 °C for 1 h, when no more nitrogen was evolved. A portion was evaporated *in vacuo* to give (±)-2βH,4aα,4bβ,8aα,10aβ-*tetradecahydro*-1,1-*dimethyl*-7-(1-*isocyanato*-2-*methylethyl*)*phenanthrene* (9) which crystal-

lised from acetone as prisms, m.p. 90—92° (Found: C, 79.35; H, 11.05; N, 4.3%; *m/e*, 303. $C_{20}H_{33}NO$ requires C, 79.15; H, 10.95; N, 4.6%; *M*, 303), τ 9.23 (3 H, s, 1-Me), 9.13 (3 H, s, 1-Me), and 8.72 (6 H, s, CMe_2·NCO).

Reduction of the Isocyanate (9) *with Lithium Aluminium Hydride*.—The xylene solution from the preceding experiment was added slowly to a suspension of lithium aluminium hydride (2.5 g) in ether (30 ml) and the mixture was left overnight at room temperature. Ethyl acetate (20 ml), water (25 ml), and sodium potassium tartrate (20 g) in water (50 ml) were added and the solution was left to stand for 1 h. The product was recovered in ether and isolated as the *hydrochloride* of (±)-2β*H*,4aα,4bβ,8aα,10aβ-*tetradecahydro*-α,α,8,8-*tetramethylphenanthren*-2-*ylmethyl*(*methyl*)-*amine* (10) which crystallised from ethanol as prisms (1.13 g), m.p. *ca.* 295—304° (decomp.) (Found: C, 73.0; H, 11.6; N, 4.3. $C_{20}H_{38}ClN$ requires C, 73.25; H, 11.4; N, 4.6%), $\nu_{max.}$ 2 440 cm^{-1}; τ 9.22 (3 H, s, 8-Me), 9.12 (3 H, s, 8-Me), 7.42br (3 H, s, NMe), *ca.* 8.66 (6 H, s, CMe_2·N), and *ca.* 0.9br (1 H, NH).

Evaporation of the residual ether solution *in vacuo*, followed by chromatography of the residue on alumina (50 g), and elution with ethyl acetate–light petroleum (7 : 93) gave the alcohol (7) (107 mg), m.p. 127—128°, identical (i.r. and n.m.r. spectra) with the specimen prepared above.

Treatment of a solution of the hydrochloride in hot water with an excess of 2N-potassium hydroxide followed by extraction with ether and recovery, gave the free amine (10) as an oil, $\nu_{max.}$ 3 330br cm^{-1}; τ 9.20 (3 H, s, 8-Me), 9.12 (3 H, s, 8-Me), 9.02 (6 H, s, CMe_2·NHMe), and 7.71 (3 H, s, NMe).

Hofmann Elimination of the Amine (10).—The amine (950 mg), anhydrous potassium carbonate (8.5 g), and methyl iodide (10 g) were heated in ethanol under reflux for 49 h, cooled, and filtered. The combined filtrate and washings were evaporated *in vacuo* and the semi-solid residue was dissolved in chloroform, washed with water, dried, and chromatographed on silver nitrate–alumina (10% $AgNO_3$; 200 g). Elution with ether–light petroleum (1 : 99) gave (±)-2β*H*,4aα,4bβ,8aα,10aβ-*tetradecahydro*-1,1-*dimethyl*-7-(1-*ethoxy*-2-*methylethyl*)*phenanthrene* (11) as a gum (35 mg) which sublimed at 60 ° (bath) and 10^{-3} mmHg (Found: C, 82.1; H, 12.55%; *m/e*, 306. $C_{21}H_{38}O$ requires C, 82.3; H, 12.5%; *M*, 306), τ 9.22 (3 H, s, 1-Me), 9.15 (3 H, s, 1-Me), 8.93 (6 H, s, CMe_2·OR), 8.79 (3 H, t, *J* 7 Hz, OCH_2·*Me*), and 6.65 (2 H, q, *J* 7 Hz, O·CH_2Me).

Elution with ether–light petroleum (2 : 98) afforded (±)-4aβ,4bα,8aβ,10aα-*tetradecahydro*-1,1-*dimethyl*-7-(1-*methylethylidene*)*phenanthrene* (15) (homogeneous by g.l.c.) which crystallised from acetone as plates (138 mg), m.p. 77—78° (Found: C, 87.7; H, 12.4%; *m/e*, 260. $C_{19}H_{32}$ requires C, 87.6; H, 12.4%; *M*, 260), τ 9.22 (3 H, s, 1-Me), 9.12 (3 H, s, 1-Me), 8.35 (6 H, s, $=CMe_2$), *ca.* 8.1 (*ca.* 2 H, m) and *ca.* 7.38 (4 H, m) (2 × allylic CH_2), and no olefinic H.

Elution with ether–light petroleum (3 : 97) gave (±)-4aβ,4bα,7β*H*,8aβ,10aα-*tetradecahydro*-1,1-*dimethyl*-7-(1-*methylvinyl*)*phenanthrene* (16) (310 mg) (homogeneous by g.l.c.) which sublimed at 50 °C (bath) and 0.1 mmHg, $[\alpha]_D^{25}$ 0°, no c.d. curve (Found: C, 87.5; H, 12.25%; *m/e*, 260. $C_{19}H_{32}$ requires C, 87.6; H, 12.4%; *M*, 260), $\nu_{max.}$ 888 and 1 640 cm^{-1}; τ 9.21 (3 H, s, 1-Me), 9.12 (3 H, s, 1-Me), 8.31 (3 H, t, *J* 1 Hz, *Me*C=CH_2), and 5.35 (2 H, m, $=CH_2$). Irradiation at the frequency of the signal at τ 5.35 caused the triplet at τ 8.31 to collapse to a singlet.

Ozonolysis of the Olefin (15).—The olefin (60 mg) in ethyl acetate (30 ml) was cooled to −78 °C and treated with an excess of ozone. Nitrogen was passed through the solution for 15 min, then it was allowed to warm up to 0 °C, and was hydrogenated with 5% palladised charcoal (60 mg) until uptake of hydrogen ceased. Recovery gave (±)-4aα,4bβ,-8aα,10aβ-*dodecahydro*-8,8-*dimethylphenanthren*-2-*one* (17) (50 mg) (homogeneous by g.l.c.) which crystallised from methanol as cubes, m.p. 80–83°, no c.d. curve (Found: C, 81.75; H, 11.25%; *m/e*, 234. $C_{16}H_{26}O$ requires C, 82.0; H, 11.2%; *M*, 234), $\nu_{max.}$ ($CHBr_3$) 1 709 cm^{-1}; τ 9.20 (3 H, s, 8-Me), 9.08 (3 H, s, 8-Me), and *ca.* 7.8 (4 H, m, CH_2COCH_2).

Ozonolysis of the Olefin (16).—The olefin (100 mg) in ethyl acetate (20 ml) was ozonised and worked-up as in the preceding experiment to give (±)-2α-*acetyl*-2β*H*,4aα,4bβ,-8aα,10aβ-*tetradecahydro*-8,8-*dimethylphenanthrene* (18) as a gum (68 mg) (homogeneous by g.l.c.) which sublimed at 60 °C (bath) and 0.01 mmHg (Found: C, 82.05; H, 11.25%; *m/e*, 262. $C_{18}H_{30}O$ requires C, 82.4; H, 11.5%; *M*, 262), $\nu_{max.}$ ($CHBr_3$) 1 710 cm^{-1}; τ 9.20 (3 H, s, 8-Me), 9.11 (3 H, s, 8-Me), and 7.88 (3 H, s, MeCO).

Dehydrogenation of the Acid (5).—The acid (300 mg) and 10% palladium–charcoal (300 mg) were heated at 300—330 °C in a stream of nitrogen for 2 h. The products were recovered in ether and evaporation *in vacuo* yielded a semi-solid (93 mg) which was purified by p.l.c. Four developments with n-hexane gave two bands; material (56 mg) from the band of higher R_F was recovered and crystallised from ethanol to afford retene as plates, m.p. 97—99° (lit.,[21] 98—99°) (Found: *m/e*, 234. Calc. for $C_{18}H_{18}$: *M*, 234), identical (u.v., n.m.r., and mass spectra) with an authentic sample.

Its picrate had m.p. 119—121° (lit.,[21] 124—125°) (Found: C, 62.15; H, 4.8; N, 8.65. Calc. for $C_{24}H_{21}N_3O_7$: C, 62.2; H, 4.6; N, 9.1%).

Material from the band of lower R_F was recovered as a gum (26 mg) and sublimed at 120 °C (bath) and 1 mmHg to yield simonellite which crystallised from ethanol as plates, m.p. 58—59° (lit.,[10] 59—60°), $\lambda_{max.}$ 233, 271sh, 278, 291sh, 310, 317, and 324 nm (ε 24 300, 6 400, 3 800, 750, 250, and 880), identical (i.r. and mass spectra and g.l.c.) with an authentic sample of simonellite.

Attempted Epimerization of the Ketone (18).—The ketone (18 mg) and potassium hydroxide (400 mg) in methanol (4 ml) were heated under reflux for 7 h in an atmosphere of nitrogen. Recovery in ether gave a gum (16 mg) shown by g.l.c. to be starting material.

Deuteriation of the Ketone (18).—The ketone (15 mg) and potassium hydroxide (340 mg) in tetrahydrofuran (2 ml) and deuterium oxide (1 ml) were heated under reflux in an atmosphere of nitrogen for 6 h. The tetrahydrofuran was removed *in vacuo* and the product, recovered in ether, was the gummy *tetradeuterioketone* (19) (14 mg) (Found: *m/e*, 266.254 4. $C_{18}H_{26}D_4O$ requires *M*, 262.254 8), $\nu_{max.}$ (film) 1 711 cm^{-1}; τ 9.22 (3 H, s, 8-Me), 9.13 (3 H, s, 8-Me), and no peak at τ 7.88 corresponding to COMe.

Decarbonylation of the Acid (12).—The acid (250 mg), lead tetra-acetate (510 mg), and copper(II) acetate (10 mg) were placed in a nitrogen-filled flask and benzene (20 ml) and pyridine (2 ml) were added. The mixture was refluxed under nitrogen for 14 h, cooled, and diluted with ether (75 ml) and water (25 ml). Iron(II) sulphate was added until the aqueous layer was saturated and the solution was acidified with 2N-hydrochloric acid. Recovery in ether afforded an oil (246 mg) which was chromatographed on

alumina (40 g). Elution with light petroleum gave an oil (107 mg) which was shown by g.l.c. and n.m.r. spectroscopy to contain (±)-1,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-dodecahydro-8,8-dimethyl-2-(1-methylethyl)phenanthrene (24) (66%), (±)-3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-dodecahydro-8,8-dimethyl-2-(1-methylethyl)phenanthrene (25) (26%), and the exocyclic olefin (15) (8%) (Found: *m/e*, 260. $C_{19}H_{32}$ requires *M*, 260), τ 9.21 (s, 8-Me), 9.12 (s, 8-Me), 9.03 (d, *J* 6 Hz, $CHMe_2$), 4.85br [s, 1-H in (25)], and 4.60br [d, *J* 5 Hz, 3-H in (24)].

Further elution with ethyl acetate–light petroleum (1 : 99) furnished a gum (28 mg) which was sublimed at 100 °C (bath) and 1 mmHg. It crystallised from light petroleum as plates of the ketone (17), m.p. 80—82°, identical (i.r. and n.m.r. spectra) with the specimen prepared above.

Reaction of the Olefinic Mixture (24), (25), *and* (15) *with Osmium Tetraoxide.*—The above olefins (106 mg) in pyridine (1 ml) were treated with osmium tetraoxide (100 mg) for 72 h. Water (15 ml), pyridine (17 ml), and sodium metabisulphite (1 g) were added and the solution was stirred overnight. The product was recovered in ether as a gum (115 mg) which was purified by p.l.c.; eight developments with ethanol–benzene (1 : 24) gave two bands.

Material from the less polar band (25 mg) was crystallised from light petroleum to give prisms of (±)-4aα,4bβ,8aα,10aβ-*dodecahydro*-8,8-*dimethyl*-2α-(1-*methylethyl*)-*phenanthrene*-1β,2β-*diol* (27), m.p. 152—153° (Found: *m/e*, 294.257 2. $C_{19}H_{34}O_2$ requires *M*, 294.255 9); τ 9.22 (3 H, s, 8-Me), 9.12 (3 H, s, 8-Me), 9.12 (3 H, d, *J* 7 Hz, Me of $CHMe_2$), 9.07 (3 H, d, *J* 7 Hz, Me of $CHMe_2$), and 6.81 (1 H, d, *J* 9.5 Hz, 1-H).

Material from the band of lower R_F was crystallised from light petroleum to afford (±)-4aα,4bβ,8aα,10aβ-*dodecahydro*-8,8-*dimethyl*-2α-(1-*methylethyl*)*phenanthrene*-2β,3β-*diol* (26) as felted needles, m.p. 138—140° (Found: *m/e*, 294.257 4. $C_{19}H_{34}O_2$ requires *M*, 294.255 9), τ 9.22 (3 H, s, 8-Me), 9.13 (3 H, s, 8-Me), 9.11 (3 H, d, *J* 7 Hz, Me of $CHMe_2$), 9.05 (3 H, d, *J* 7 Hz, Me of $CHMe_2$), and 6.37 (1 H, dd, *J* 11 and 4.5 Hz, 3-H).

Reaction of the Diol (26) *with Lead Tetra-acetate.*—The diol (29 mg) in pyridine (4 ml) was treated with lead tetra-acetate (60 mg) for 24 h. The mixture was diluted with water and the product was recovered in ether as a gum which was purified by p.l.c. with two developments in ethanol–benzene (1 : 49).

Material from the middle band gave (±)-1αH,2βH,4aα,8aβ-decahydro-2α-(2-oxo-3-methylbutyl)-5,5-dimethylnaphthalen-1β-ylacetic acid (29) as an oil (13 mg), $\nu_{max.}$ (film) 2 660 and 1 705 cm^{-1}; τ 9.20 (3 H, s, 5-Me), 9.11 (3 H, s, 5-Me), 8.92 (6 H, d, *J* 7 Hz, $CHMe_2$), and 7.65—7.25 (5 H, m, CH_2CO_2H, $COCHMe_2$, and $CH_2COCHMe_2$).

Its *methyl ester* (30), prepared with diazomethane, was an oil (Found: *m/e*, 322.250 5. $C_{20}H_{34}O_3$ requires *M*, 322.250 8), τ 9.21 (3 H, s, 5-Me), 9.12 (3 H, s, 5-Me), 8.93 (6 H, d, *J* 7 Hz, $CHMe_2$), 7.65—7.25 (5 H, m, CH_2CO_2Me, $COCHMe_2$, and $CH_2COCHMe_2$), and 6.34 (3 H, s, OMe). Irradiation at the frequency of the signal at τ 7.50 caused the doublet at τ 8.93 to collapse to a singlet.

Reaction of 8β,13βH-*Tetrahydroabietic Acid* (1) *with Concentrated Sulphuric Acid at* 0—5 °C *in the Presence of Sodium* [^{14}C]*Formate.*—Finely ground 8β,13βH-tetrahydroabietic acid (2 g) (containing 11% of its 13α-epimer) was intimately mixed with sodium formate (400 mg) and sodium [^{14}C]formate (50 μCi) in one arm of a stoppered vessel. The other arm of the vessel contained concentrated sulphuric acid (16 ml) at 0—5 °C, which was tipped onto the solid mixture, and the reaction was stirred at 0—5 °C for 50 min. The mixture was worked up in the usual manner to give the sodium salt of the acid (5) and a neutral fraction (228 mg). The [^{14}C]acid (5) (371 mg) was liberated from the sodium salt in the normal fashion and was then crystallised from acetone to give prisms, m.p. 212—214°, 4.12×10^4 disintegrations $mmol^{-1}$ s^{-1}, identical (i.r. spectrum and g.l.c.) with an authentic specimen.

Reaction of 8α,13αH-*Tetrahydroabietic Acid* (4) *with Concentrated Sulphuric Acid at* 0—5 °C.—The tetrahydroabietic acid (780 mg) (shown to contain 7% 13αH-$\Delta^{8(9)}$-dihydroabietic acid by g.l.c. and mass spectroscopy), was treated in the usual manner with concentrated sulphuric acid (10 ml), previously saturated with carbon monoxide, for 1 h at 0—5 °C, and was then poured into ice. The product was extracted with ether and separated into acidic (390 mg) and neutral fractions (115 mg) with 0.25N-sodium hydroxide solution. The extraction with excess of base also precipitated sodium salts which were collected by filtration. The salts were suspended in water, acidified with 2N-hydrochloric acid, and extracted with ether. Recovery gave a solid (89 mg), which was crystallised from acetone to give the acid (5), m.p. 212—214°, identical (i.r. spectrum and g.l.c.) with an authentic sample.

The neutral fraction was chromatographed on silica gel. Elution with light petroleum gave a gum (Found: *m/e*, 262. $C_{19}H_{34}$ requires *M*, 262).

Examination of the acidic fraction by g.l.c. gave a pattern of peaks very similar to that obtained from the acidic fraction produced by rearrangement of the acid (1).

Reaction of 8β,13αH-*Tetrahydroabietic Acid* (2) *with Concentrated Sulphuric Acid at* 0—5 °C.—The acid (600 mg) was treated with concentrated sulphuric acid (10 ml) previously saturated with carbon monoxide, at 0–5 °C as in the preceding experiment. Isolation of the products as above gave an acidic fraction (316 mg), a neutral fraction (64 mg), and a mixture of sodium salts from which solid acids were obtained (169 mg). G.l.c. of the latter showed that the mixture contained the ' third acid ' isomer (52%), the acid (5) (33%), and the acid (12) (15%). Fractional crystallisation from acetone yielded the acid (5), m.p. 212—214°, identical (g.l.c. and i.r. spectrum) with an authentic specimen.

G.l.c. of the acidic fraction showed a pattern of peaks very similar to those obtained from the rearrangement of isomeric tetrahydroabietic acids.

Reaction of 8β,13βH-*Tetrahydroabietic Acid* (1) *with Deuteriosulphuric Acid at* 0—5 °C.—The tetrahydro-acid (2 g) (containing 11% of its 13-epimer) was added to deuteriosulphuric acid (16 ml) at 0—5 °C. The latter had been previously saturated with carbon monoxide, generated *in situ* from sodium formate (200 mg). The mixture was stirred at 0—5° for 50 min and was then worked up as above by method (iii) to give a neutral fraction as a gum (270 mg) and the acids (642 mg) which on crystallisation from acetone afforded the polydeuteriated acid (5) as microprisms, m.p. 206—207° (homogeneous by g.l.c.) [Found: *m/e*, 335 (0.4%), 334 (0.9), 333 (1.7), 332 (2.3), 331 (3.6), 330 (4.1), 329 (4.7), 328 (4.7), 327 (4.2), 326 (4.0), 325 (3.0), 324 (2.1), 323 (1.3), 322 (0.9), 321 (0.5), 320 (0.4), 319 (0.3), 318 (0.5), 317 (1.0), 316 (2.4), 315 (3.6), 314 (5.6), 313 (5.8), 312 (6.1), 311 (5.6), 310 (4.0), 309 (3.7), 308 (2.4), 307 (1.9), and 306 (1.1). $C_{20}H_5D_{29}O_2$ requires *M*, 335. Calc. for $C_{20}H_{34}O_2$:

M, 306], $\nu_{max.}$ 2 650, 2 200, 2 180, 2 103, and 1 695 cm^{-1}; τ (90 MHz) 9.24w (s, 8-Me), 9.15w (s, 8-Me), 8.89vw (s, $CMe_2 \cdot CO_2H$), and 8.58 (t, CH_2 groups).

Its methyl ester crystallised from methanol as plates, m.p. 78—79°, whose mass spectrum showed molecular ions at all whole-number masses from *m/e* 349 to 320 (Found: *m/e*, 349.453 3. $C_{21}H_7D_{29}O_2$ requires *M*, 349.453 6. Calc. for $C_{21}H_{36}O_2$: *M*, 320), $\nu_{max.}$ 2 195, 2 105, and 1 735 cm^{-1}; τ (90 MHz) 9.25w (s, 8-Me), 9.16w (s, 8-Me), 8.92vw (s, $CMe_2 \cdot CO_2Me$), and 6.38 (3 H, s, OMe).

Concentration of the mother liquors from the polydeuteriated acid (5) afforded a crystalline solid (159 mg) which which shown by g.l.c. to be a mixture of the polydeuteriated acid (5) (39%) and the polydeuteriated analogue of the ' third acid ' (58%). Fractional crystallisation from acetone furnished the latter as rods (homogeneous by g.l.c.), m.p. 193—194° (decomp.) (Found: *m/e*, 332.418 0. $C_{20}H_8D_{26}O_2$ requires *M*, 332.419 1), $\nu_{max.}$ 2 660, 2 560, 2 185, 2 105, and 1 700 cm^{-1}; τ (90 MHz) 9.31 (s, Me) and 8.89w (s, $CMe_2 \cdot CO_2H$).

The mass spectrum of its methyl ester contained the following molecular ions [Found: *m/e*, 346 (1.5%), 345 (0.9), 344 (2.0), 343 (1.5), 342 (2.0), 341 (2.3), 340 (2.6), 339 (2.2), 338 (0.5), 337 (1.4), 336 (1.6), 335 (1.0), 334 (0.8), 333 (0.6), 331 (1.0), 330 (1.5), 329 (2.4), 328 (2.7), 327 (2.1), 326 (4.0), 325 (4.1), 324 (2.4), 323 (3.0), 322 (1.0), 321 (2.0), and 320 (1.1). $C_{21}H_{10}D_{26}O_2$ requires *M*, 346. Calc. for $C_{21}H_{36}O_2$: *M*, 320].

The crude neutral fraction was a mixture of polydeuteriated saturated hydrocarbons [Found: *m/e*, 291 (1.8%), 290 (4.8), 289 (6.8), 288 (10.7), 287 (15.9), 286 (17.9), 285 (17.1), 284 (20.8), 283 (16.2), 282 (14.8), 281 (11.8), 280 (8.8), 279 (7.3), 278 (4.8), 277 (3.8), 276 (1.7), 275 (2.3), 274 (4.7), 273 (8.5), 272 (12.9), 271 (20.1), 270 (24.1), 269 (27.1), 268 (25.6), 267 (23.6), 266 (17.9), 265 (12.4), 264 (10.7), 263 (7.6), and 262 (3.5). $C_{19}H_5D_{29}$ requires *M*, 291. $C_{19}H_{34}$ requires *M*, 262].

Reaction of 8β,13βH-*Tetrahydroabietic Acid* (1) *with Antimony Pentafluoride–Fluorosulphonic Acid*—(a) *At* 0—5 °C. The tetrahydro-acid (1.03 g) (containing 11% of its 13-epimer), was added in portions to antimony pentafluoride–fluorosulphonic acid (1 : 1; 12.5 g) at 0 °C. The deep orange solution, which was formed immediately, was stirred at 0—5 °C for 1 h and was then poured onto ice (50 g). Recovery in ether gave a gummy acidic fraction (402 mg) and a neutral fraction (526 mg).

The acidic fraction was chromatographed on silica gel (100 g) and elution with ethyl acetate–light petroleum (1 : 19) afforded an oil (153 mg), shown by g.l.c. to be a complex mixture of products of short retention time (Found: *m/e*, 306. $C_{20}H_{34}O_2$ requires *M*, 306).

The neutral fraction was chromatographed on silica gel (100 g) and the material eluted with ethyl acetate–light petroleum (1 : 99) was rechromatographed on alumina (50 g). Elution with light petroleum gave an oil (157 mg) [Found: *m/e*, 262 and 260 (ratio 65 : 35). $C_{19}H_{34}$ requires *M*, 262. $C_{19}H_{32}$ requires *M*, 260]; τ no olefinic protons.

(b) *At* −30 °C. The acid (523 mg) was added to antimony pentafluoride–fluorosulphonic acid (6 g) at −30 °C and the resultant solution was stirred at this temperature for 1 h. Work-up as described above afforded an acidic fraction (298 mg) and a neutral fraction (243 mg).

The crude acid was chromatographed on silica gel (50 g). Elution with ethyl acetate–light petroleum (1 : 49) yielded a gum (136 mg) which on crystallisation from acetone afforded the acid (1), m.p. 178—180°, identical (g.l.c., n.m.r., and i.r. spectra) with starting material.

(c) *At* −70 °C. The acid (1.06 g) (containing 11% of its 13-epimer) was added in portions to a mixture of antimony pentafluoride–fluorosulphonic acid (10 g) and liquid sulphur dioxide (5 ml) at −70 °C and the mixture was stirred for 1 h at −70 °C. Work-up as described above gave an acidic fraction (921 mg) and a neutral fraction (79 mg).

The acidic fraction crystallised from acetone yielding prisms of pure 8β,13βH-tetrahydroabietic acid (1) (homogeneous by g.l.c.), m.p. 186—187° (lit.,[1] 185.5—186°) (Found: *m/e*, 306. Calc. for $C_{20}H_{34}O_2$: *M*, 306).

Reaction of the Acid (5) *with Concentrated Sulphuric Acid at* 0—5 °C.—The acid (1 g) was added to a stirred mixture of concentrated sulphuric acid (8 ml) and sodium formate (70 mg) which was kept at 0—5 °C for 26 h and then poured onto ice (50 g). Recovery in ether yielded an acidic solid (853 mg), which was crystallised from acetone to give the acid (5) as prisms, m.p. 211—213°, identical (g.l.c. and i.r. spectrum) with starting material, and a neutral gum (98 mg) (Found: *m/e*, 262. $C_{19}H_{34}$ requires *M*, 262).

The residue obtained by evaporating the mother-liquors was methylated in the usual manner with diazomethane to give a mixture of methyl esters which were shown by g.l.c. to contain at least eight compounds, of which the esters (6) and (13) were the major components.

The methyl esters (565 mg) were reduced with lithium aluminium hydride (75 mg) in dry ether at room temperature for 1 h. Work-up in the usual manner followed by chromatography of the crude product on silica gel (100 g) and elution with ethyl acetate–light petroleum (1 : 49) gave a mixture of unchanged methyl esters (134 mg) as a gum shown by g.l.c. to contain at least eight compounds with the major product (45%) having a retention time corresponding to that of the ester (13).

Elution with ethyl acetate–light petroleum (1 : 19) afforded a mixture of alcohols (340 mg).

The above mixture of esters was reduced with lithium aluminium hydride (100 mg) in ether (25 ml) under reflux for 24 h. The recovered alcohols (131 mg) in acetone (30 ml) were oxidised with an excess of Jones reagent at room temperature for 2.5 h. Recovery in ether gave a gum (121 mg) which crystallised from acetone as prisms of the acid (12), m.p. 179—180°, identical (i.r. spectrum and g.l.c.) with an authentic sample.

Reaction of the Acid (5) *with Deuteriosulphuric Acid at* 0—5 °C.—The acid (948 mg) was finely powdered and added with stirring to deuteriosulphuric acid (8 ml) at 0—5 °C. The latter had been saturated with carbon monoxide by the addition of sodium formate (70 mg) and the reaction was continued at 0—5 °C for 26 h. The acidic product was isolated in the usual manner, and was crystallised from acetone to furnish unchanged (5) (669 mg), m.p. 210.5—212°, identical (i.r. and mass spectra, and g.l.c.) with starting material.

The mother-liquors were evaporated *in vacuo*, methylated with ethereal diazomethane, and reduced with lithium aluminium hydride (15 mg) in ether for 1 h at room temperature. Work-up in the usual manner afforded an oil (240 (mg) which was chromatographed on silica gel (40 g). Elution with ethyl acetate–light petroleum (1 : 49) yielded unchanged methyl esters (62 mg), shown by g.l.c. to be a mixture of six compounds with the major product (85%)

having a retention time corresponding to that of the ester (13). Further elution gave a mixture of alcohols (162 mg), $\nu_{max.}$ ($CHCl_3$) 3 350 cm^{-1}.

The above methyl esters were reduced with lithium aluminium hydride (100 mg) in refluxing ether for 24 h and the resultant mixture of alcohols in acetone (25 ml) was treated with an excess of Jones reagent at room temperature for 2.5 h. Work-up in the usual manner afforded the polydeuteriated acid (12) (homogeneous by g.l.c.) which crystallised from acetone as prisms, m.p. 170—172°, $\nu_{max.}$ 2 660, 2 220, 2 200, 2 180, 2 100, and 1 698 cm^{-1}; τ (90 MHz) 9.24w (s, 8-Me), and 9.14w (s, 8-Me); no isopropyl signal.

The mass spectrum of its methyl ester (13) contained the following molecular ions [Found: *m/e*, 349.493 0 (2.1%), 348 (7.8), 347 (14.0), 346 (19.8), 345 (39.5), 344 (61.5), 343 (83.5), 342 (86.8), 341 (85.0), 340 (66.0), 339 (46.0), 338 (39.5), 337 (30.4), 336 (24.2), 335 (16.8), 334 (17.7), 333 (9.6), 332 (7.6), 331 (8.5), 330 (13.0), 329 (12.8), 328 (15.6), 327 (19.8), 326 (19.7), 325 (17.4), 324 (10.8), 323 (8.4), 322 (8.2), 321 (6.8), and 320 (5.2). $C_{21}H_7D_{29}O_2$ requires *M*, 349.453 6. $C_{21}H_{36}O_2$ requires *M*, 320], τ 90 (MHz) 9.25w (s, 8-Me), 9.15w (s, 8-Me), and 6.34 (3 H, s, OMe); no isopropyl signal.

Reaction of the Acid (12) *with Deuteriosulphuric Acid at* 0—5 °C.—The acid (200 mg) was allowed to react with deuteriosulphuric acid (3 ml) at 0—5 °C for 1.5 h. Isolation of the products (as above) gave an acidic fraction (157 mg) and a neutral fraction (31 mg). The former was identified as starting material by g.l.c., i.r., and mass spectrometry (Found: *m/e*, 306. Calc. for $C_{20}H_{34}O_2$: *M*, 306).

We thank Professor E. Ghigi for an authentic sample of simonellite, Drs. P. M. Scopes and R. J. Pryce for c.d. and o.r.d. measurements, respectively, Mr. T. E. Etherington for technical assistance, and the S.R.C. for maintenance awards (M. R. F. and R. E. M.).

[9/139 *Received*, 30*th January*, 1979]

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